RENTLY DRIVEN MOLECULAR VIBRATIONS AND LIGHT MODU

E. Garmire, F. Pandarese[**], and C. H. Townes
Massachusetts Institute of Technology

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Theories of Raman masers have previously concentrated attention on the individual molecular process of Raman scattering, and on the normal Raman emission.[(1), (2), (3), (4)] Very intense maser light beams in dense matter produce interesting higher-order Raman effects, particularly through excitation of intense coherent molecular oscillations at infrared frequencies. These modulate the original light and its Raman-scattered radiation, producing Stokes and anti-Stokes lines of many orders, frequently without a threshold condition for generation, and in some cases with highly directional radiation patterns.

A molecule in an oscillating electric field E vibrates due to a force of the form $\frac{1}{2} \frac{d\alpha}{dx} E^2$ where α is the polarizability (considered isotropic for simplicity) and x is a vibrational coordinate. There is an additional force associated with the interaction between the induced dipole moments of adjacent molecules. If the polarizabilities of the two molecules are α_1, and α_2, then their interaction energy is approximately $\frac{2\alpha_1\alpha_2}{d^3} E^2$, where d is the intermolecular distance. The corresponding force driving the vibration of molecule 2 is $\frac{2\alpha_1}{d^3} \frac{d\alpha_2}{dx} E^2$. Since both forces have the same dependence on the electric field, they will be combined into an effective force $F = fE^2$.

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** On Leave of absence from C. N. E. N. Laboratori Nazionali del Sincrotrone, Frascati, Italy.

If the electric field is a light wave of the form

$$\vec{E} = \vec{E}_o \cos(\omega_o t - \vec{k}_o \cdot \vec{r}) + \vec{E}' \cos(\omega' t - \vec{k}' \cdot \vec{r} + \varphi')$$

where $\vec{r}$ is the position vector for the molecules, then F has a frequency component oscillating at $\omega_o - \omega'$ which is resonant when $\omega_o - \omega' = \pm\omega_r$, the natural molecular vibrational frequency. If this vibration is subject to a molecular damping force $R\dot{x}$, then on resonance

$$x = \frac{f\,\vec{E}_o \cdot \vec{E}'}{R(\omega_o - \omega')} \sin\left[(\omega_o - \omega')t - (\vec{k}_o - \vec{k}') \cdot \vec{r} - \varphi'\right].$$

This driven molecular vibration results in an oscillating electric dipole moment

$$\vec{\mu} = x\,\frac{d\alpha}{dx}\,\vec{E} = \frac{f\frac{d\alpha}{dx}\,\vec{E}_o \cdot \vec{E}'}{R(\omega_o - \omega')} \sin\left[(\omega_o - \omega')t - (\vec{k}_o - \vec{k}') \cdot \vec{r} - \varphi'\right]\vec{E}.$$

The rate of energy exchange between the dipole moment and the component of the field of frequency ω' is given by $\vec{P}' = -\overline{\frac{d\vec{\mu}}{dt} \cdot \vec{E}'}$, where the average is taken over time. From the above expressions, the power delivered to E' from an initial beam E_o is $P' = \frac{f}{4R}\,\frac{d\alpha}{dx}\,\frac{\omega'}{\omega_o - \omega'}\,(\vec{E}_o \cdot \vec{E}')^2$. Thus, for the Stokes radiation, where $\omega' = \omega_o - \omega_r$, $P' > 0$ and E' is amplified; while for anti-Stokes radiation, where $\omega' = \omega_o + \omega_r$, E' loses energy.

Anti-Stokes radiation can be amplified if a radiation field is considered of the form

$$\vec{E} = \vec{E}_o \cos(\omega_o t - \vec{k}_o \cdot \vec{r}) + \vec{E}_{-1} \cos\left[(\omega_o - \omega_r)t - \vec{k}_{-1} \cdot \vec{r} + \varphi_{-1}\right] + \vec{E}_1 \cos\left[(\omega_o + \omega_r)t - \vec{k}_1 \cdot \vec{r} + \varphi_1\right].$$

The same treatment shows that $P_{-1} = \frac{f}{4R}\,\frac{d\alpha}{dx}\,\frac{\omega_o - \omega_r}{\omega_r}\left\{(\vec{E}_o \cdot \vec{E}_{-1})^2 + (\vec{E}_o \cdot \vec{E}_1)(\vec{E}_o \cdot \vec{E}_{-1}) \cos\left[(2\vec{k}_o - \vec{k}_1 - \vec{k}_{-1}) \cdot \vec{r} + \varphi_1 + \varphi_{-1}\right]\right\}$ and

$$P_1 = \frac{f}{4R}\,\frac{d\alpha}{dx}\,\frac{\omega_o + \omega_r}{\omega_r}\left\{-(E_o \cdot E_1)^2 - (E_o \cdot E_1)(E_o \cdot E_{-1}) \cos\left[(2\vec{k}_o - \vec{k}_1 - \vec{k}_{-1}) \cdot \vec{r} + \varphi_1 + \varphi_{-1}\right]\right\}.$$

Thus, if $E_{-1} > E_1$, E_1 may be amplified when $2\vec{k}_o - \vec{k}_{-1} - \vec{k}_1 = 0$, and cos $(\varphi_1+\varphi_{-1}) < 0$. If $\varphi_1+\varphi_{-1} = \pi$, E_1 will have the largest gain; while in the direction $\vec{k}_{-1}$, the gain in E_{-1} will be decreased by the term $E_1\, E_{-1}$ in P_{-1}. In this case the molecular oscillation x is proportional to $E_{-1} - E_1$, since the two fields drive the molecule in opposite phase. However, if there is a non-linear damping of the molecular motion, E_{-1} may possibly be enhanced rather than diminished, since such losses would be minimized in this particular direction.

The generation of E_1 may be looked at as caused by a modulation of E_o in the medium due to the large coherent molecular oscillation set up by E_o and E_{-1} and the resulting variation in index of refraction at frequency ω_r. Such modulation produces sidebands on any radiation present, and hence if threshold conditions for generation of E_{-1} are met, many frequencies can be produced without a further threshold.

A classical treatment of these phenomena is quite adequate in most cases, although of course detailed molecular properties can be accurately calculated only by a quantum mechanical approach to molecular structure. From a macroscopic view, the behavior of the material may be described by a non-linear polarization associated with a susceptibility of the form $\chi = \chi_o + \chi' E^2 + \cdots$, where χ' has a highly resonant imaginary component at ω_r. The imaginary component or 90^o phase shift of the polarization is essential in producing the above behavior. The magnitude of χ' is greater at ω_r than for frequencies off resonance by $Q = \frac{\omega_r}{\Delta\omega}$, where $\Delta\omega$ is the half width of the vibrational frequency at half-maximum intensity. This factor Q can be as large as about 1000, so that these non-linear effects can be unusually large at resonance.

There is already considerable experimental information available on Raman radiation in very intense fields.[5,6,7] The above ideas seem to allow a fairly detailed understanding of effects so far reported and lead to the following conclusions, some of which correspond to established experimental observations.

1. Stokes radiation, of frequency $\omega_o - \omega_r$, in first approximation is emitted diffusely, its intensity varying with angle and polarization roughly as $(E_o \cdot E_{-1})^2$. Additional angular variation occurs because of differing path lengths in the beam over which amplification can occur. There will also be a threshold for the generation of E_{-1} in any given direction since both the power generated and the losses are proportional to E^2_{-1}.

2. Anti-Stokes radiation, of frequency $\omega_o + \omega_r$, is emitted in cones in the forward direction around the initial beam at an angle θ_1, given for small angles by $\theta_1^2 = \frac{1}{n} \frac{\omega_o - \omega_r}{\omega_o + \omega_r} \left[\Delta n_1 - \Delta n_{-1} + \frac{\omega_r}{\omega_o}(\Delta n_{-1} + \Delta n_1)\right]$ where n is the index of refraction, Δn_{-1} the difference in the indices of refraction for ω_o and $\omega_o - \omega_r$, Δn_1 that for ω_o and $\omega_o + \omega_r$. All of these quantities are positive for normal dispersion. The corresponding Stokes radiation which interacts with this anti-Stokes light occurs at an angle $\theta_{-1} = \frac{\omega_o + \omega_r}{\omega_o - \omega_r} \theta_1$. Since these beam angles are expressed within the medium, refraction may change them upon emergence from the medium. These angles are typically a few degrees, and the anti-Stokes radiation observed occurs at angles consistent with the above to within the rather unsatisfactory accuracy with which Δn_1 and Δn_{-1} are known. There is no threshold condition for the generation of this radiation beyond the existence of E_{-1} at an appropriate angle, since the power gain is proportional to E_1, while losses are proportional to $E_1{}^2$.

3. Anti-Stokes radiation will not usually build up in a Raman maser with plane parallel reflectors perpendicular to the initial beam. Because of dispersion, the wave vector relation cannot be satisfied by E_o and the parallel E_{-1} wave, which builds up by the first process discussed above in the direction of maximum gain at the expense of other possible Stokes waves.

4. A field E_{-2} at frequency $\omega_o - 2\omega_r$ can be emitted diffusely by a process generating power proportional to $E_{-1}^2 E_{-2}^2$ essentially identical with that for the generation of E_{-1}. In addition it may be produced through modulation of E_{-1} by the oscillations in dielectric constant due to E_o and E_{-1}, giving a power generation proportional to $E_o (E_{-1})^2 E_{-2}$. The latter case, which has no threshold provided E_{-1} is present, is the more important in generation of Raman radiation by intense beams outside a cavity, since in any one direction $|E_{-2}| < |E_o|$. It requires $\vec{k}_o - \vec{k}_{-1} = \vec{k}'_{-1} - \vec{k}_{-2}$, where the wave vectors $\vec{k}_{-1}$ and $\vec{k}'_{-1}$ may be differently oriented but both correspond to frequencies $\omega_o - \omega_r$. This equation cannot usually be satisfied in a dispersive medium if E_{-1} is in the same direction as E_o. Hence, the former mechanism, which has a threshold, is probably the more important in a resonant cavity. Similar mechanisms can generate other Stokes beams of frequencies $\omega_o - n\,\omega_r$. The strongest such radiation will usually be due to the modulation processes, which require no threshold condition, and will be diffusely emitted unless there is feedback by reflection of the wave.

5. Radiation of frequency $\omega_o + 2\,\omega_r$ is produced without threshold effects by vibrational modulation of $\omega_o + \omega_r$, and is emitted in the direction specified by $\vec{k}_o - \vec{k}_{-1} = \vec{k}_2 - \vec{k}_1$. For normal materials, there is a $\vec{k}_{-1}$ and a $\vec{k}_2$ which will

satisfy this equation, the angle between $\vec{k}_o$ and $\vec{k}_2$ being of the order of $2\Theta_i$. Other anti-Stokes beams of frequency $\omega_o + n\,\omega_r$ are similarly generated in cones about the original beam.

6. Higher order processes can produce weaker cones of both Stokes and anti-Stokes Raman light in varying directions. For example, the equation $\vec{k}_o - \vec{k}_1 = \vec{k}_{-2} - \vec{k}_{-1}$ specifies one such case, where $\vec{k}_{-1}$ is a ray of the backward diffusely scattered Stokes light, and $\vec{k}_{-2}$ corresponds to generation of a beam of frequency $\omega_o - 2\,\omega_r$ which can be at large angles or in the backward direction, depending on the dispersion.

7. The fractional power gain per unit length for diffusely directed generation of E_{-1} (ignoring molecular interaction) is: $a = \frac{\rho\,\pi}{c\,m\,R}\left(\frac{d\alpha}{dx}\right)^2 \frac{\omega_o - \omega_r}{\omega_r} E_o^2$ where is the density of the material and m the reduced mass. For a diatomic molecule, R would be $2\pi m \Delta\nu$ where $\Delta\nu$ is the half-width of the Raman resonance. Here homogeneous broadening has been assumed; extension to the inhomogeneous case is straight-forward and will give the same final result in terms of $\Delta\nu$ for this particular expression. For typical cases, if the initial beam E_o has 100 megawatts power per square centimeter, a is of the order of 5 cm^{-1}. This type of gain has been formulated already in terms of matrix elements.(1) (2) (3) (4) As usual in masers, the gain results in an emission line appreciably narrower than the usual spontaneously emitted Raman radiation.

If the fields E_{-1} and E_1 are initially $E_{-1}(0)$ and 0 respectively, and if each has a fractional power loss b per unit length in the medium due to other effects, the build-up thereafter of the two interacting waves in a distance L will have the form

$$E_1 = E_{-1}(0)\,\frac{aL}{2}\,e^{-\frac{bL}{2}}$$

$$E_{-1} = E_{-1}(0)\left(\frac{aL}{2} + 1\right)e^{-\frac{bL}{2}}$$

Thus for $\frac{aL}{2} > 1$, E_1 becomes comparable to E_{-1}. Usually $\frac{bL}{2} << 1$ for pertinent cases.

8. Field strengths E_o and E_{-1} corresponding to powers of 50 megawatts/cm^2 each produce coherent molecular vibration amplitudes x of the order of 10^{-5} of the molecular bond lengths at the resonant frequency ω_r, or about 10^{-3} of that due to one quantum of excitation. Since there are planes specified by $(\vec{k}_o - \vec{k}_{-1}) \cdot \vec{r} = 0$ in which the oscillations are all in phase, the material will usually expand by about the fractional amount 10^{-5} due to the molecular stretching. This macroscopic expansion can take place only much more slowly than the molecular period of about 10^{-14} sec., but will partially follow the envelope of the 3×10^{-8} sec. pulses in which such intense light is normally used.

9. These slower expansions and spatial variations in the dielectric constant of the medium as well as those oscillating at infrared frequencies can produce a number of other interesting scattering effects, somewhat like those calculated by Raman and Nath.[8] Use of this type of approach and a gross Kerr constant for the medium give good agreement in producing Raman light of the observed intensity if there is an effective Kerr constant at frequency ω_r about 100 times the normal size for a symmetric molecule. This is the order of the increase expected from the Q of the resonance, and gives fractional dielectric variations in the material of about 10^{-5}, as found above.

10. The intensity of these Raman lines is much affected by inter-molecular interactions. The force dependent on the polarizability of adjacent molecules and the resulting dipolar interaction can be dominant in driving the molecular vibrations if $4\alpha_1 > d^3$. This is indicated in the experimental observation that

the $C_6 H_6$ lines are more intense when the highly polarizable molecule CS_2 is mixed with $C_6 H_6$ than in the pure material.[7] There are, furthermore, additional important interactions between two adjacent molecules. The polarizability of one molecule can be modulated by vibrations of an adjacent molecule an amount comparable with that due to its own vibration. Modulation by this mechanism at a sum or difference of molecular frequencies is also possible, but is a smaller effect.

(11) If the molecules have a fixed dipole moment which is a function of the vibrational coordinate x, and if they are partially aligned, they may emit directional infrared radiation at frequency ω_r. The same effect can occur through a dipole moment induced by a strong static electric field parallel to E_o. However, for such radiation to build up over a large volume, one must have $\vec{k}_o - \vec{k}_{-1} = \vec{k}_r$, or $\cos \theta_r = 1 + \frac{\Delta n_r}{n} \frac{\omega_o - \omega_r}{\omega_o} + \frac{\Delta n_{-1}}{n} \frac{(\omega_o - \omega_r)^2}{\omega_o \omega_r}$ where θ_r is the angle between $\vec{k}_o$ and $\vec{k}_r$, and Δn_r is the difference in indices of refraction for ω_o and ω_r taken positive for normal dispersion. Hence θ_r can be real in isotropic media only if anomalous dispersion is present or for a non-dispersive medium. From such media, or from anisotropic crystals, or from material of finite extent, it would appear possible to couple out infrared radiation at frequency ω_r.

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